Anisotropic Magnetoresistance in Charge-Ordering $Na_{0.34}(H_3O)_{0.15}CoO_2$: Strong Spin-Charge Coupling and Spin Ordering

C. H. Wang[1], X. H. Chen[1],*, and G. Wu[1], T. Wu[1], H. T. Zhang[1], J. L. Luo[2], G. T. Liu[2] and N. L. Wang[2]

1. Hefei National Laboratory for Physical Science at Microscale and Department of Physics,
University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China and
2. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics,
Chinese Academy of Science, Beijing 100080, People's Republic of China
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Angular-dependent in-plane magnetoresistance (AMR) for single crystal $Na_{0.34}(H_3O)_{0.15}CoO_2$ with charge ordering is studied systematically. The anisotropic magnetoresistance shows a twofold symmetry at high temperature with rotating H in the Co-O plane, while a sixfold symmetry below a certain temperature (T_ρ). At T_ρ, the symmetry of AMR changes from twofold to fourfold with rotating magnetic field (H) in the plane consisting of the current and c-axis. The variation of AMR symmetry with temperature arises from the subtle changes of the spin structure. These results give a direct evidence for the itinerant electrons directly coupled to the localized spins.

The layered sodium cobaltate Na_xCoO_2 has become one of the focus in research due to the discovery of superconductivity with $T_c \sim 5$ K in $Na_{0.35}CoO_2 \cdot 1.3H_2O$.[1] In fact, the phase diagram in this system is very rich[2, 3, 4] and one has observed charge order and several complicated magnetic orders in addition to superconductivity.[5, 6, 7] Recently, many anomalous properties were observed in this system. The angle-resolved photoemission spectroscopy(ARPES) experiments indicates that in $Na_{0.7}CoO_2$ the well-defined quasiparticle peaks only exist in low temperature when a coherent transport forms along c-axis.[8] Such peculiar behaviors make one believe that Na_xCoO_2 could be regarded as a new prototype for studying the doped Mott insulator.

Na_xCoO_2 system shows complicated magnetic structure. The bulk antiferromagnetism (AF) with the ordering moment perpendicular to Co-O plane was observed in $Na_{0.82}CoO_2$[9]. In $Na_{0.75}CoO_2$, the ferromagnetic correlation within the cobalt layer and AF correlation between the cobalt layers were observed with spin direction along c-axis.[10, 11] Neutron diffraction and NMR studies indicate that there exist two distinct Co sites with different magnetic moments in $Na_{0.5}CoO_2$ and antiferromagnetic ordering occurs below $T_{c1} \sim 87$ K.[12, 13] However, two different magnetic structures are proposed by Yokoi et al.[12] and Gasparovic et al.[13], respectively. Gasparovic et al. proposed that magnetic moment of Co^{4+} ions that is magnetic (in the S=1/2 low spin state) aligns antiferromagnetically, the rows of Co^{4+} ions alternate with rows of Co^{3+} ions (in the S=0 spin state) that are nonmagnetic. Yokoi et al. believed that the spin structure of $Na_{0.5}CoO_2$ has three axis, two axes are $Co^{3.5-\delta} - Co^{3.5-\delta}$ and the other one is $Co^{3.5+\delta} - Co^{3.5+\delta}$. The large moments of $Co^{3.5+\delta}$ sites align antiferromagnetically with spin direction in Co-O plane. The small moments of $Co^{3.5-\delta}$ sites is along c-axis and their in-

terplane correlation is antiferromangetic. The magnetic structure for $Na_{0.5}CoO_2$ is open question.

The oxonium ions, $(H_3O)^+$, can occupy the same crystallographic sites of the Na ions when the Na_xCoO_2 crystal is immersed in distilled water.[14, 15] Intercalation of $(H_3O)^+$ makes the Co valence to be lower than theoretical value estimated directly from Na content. Much research focused on the effect of oxonium ions[4, 15] in Na_xCoO_2 system, so that superconducting phase diagram is revised. Oxidation state of Co for superconducting sample is very close to 3.5 of $Na_{0.5}CoO_2$ due to intercalation of oxonium ions instead of about 3.7.[16] One should take the charge ordering insulator with Co oxidation state of ~ 3.5 as parent compound for the superconductor. Therefore, understanding on microscopic magnetic structure of $Na_{0.5}CoO_2$ is very important to understand the charge ordering behavior and superconducting mechanism.

Magnetoresistance (MR) provides new insight into the coupling between charges and background magnetism. This is particularly valuable because, as shown in this work, small magnetic moments order in the background of magnetic ordering with large magnetic moments, and such ordering is difficultly detected by magnetization measurement. In this paper, we studied AMR of $Na_{0.34}(H_3O)_{0.15}CoO_2$ crystal with the same charge ordering as that in $Na_{0.5}CoO_2$.[17] Change of AMR symmetry from twofold to sixfold is observed with rotating H in the Co-O plane at a certain temperature (T_ρ). At T_ρ, symmetry of AMR changes from twofold to fourfold with rotating magnetic field (H) in the plane consisting of the current (I) and c-axis. Such symmetry change of AMR can be well understood by spin ordering of $Co^{3.5-\delta}$ sites with small magnetic moments below T_ρ. Our results support the model proposed by Yokoi et al.[12] These results give a direct evidence for the itinerant electrons directly coupled to the localized spins.

High quality single crystal $Na_{0.34}(H_3O)_{0.15}CoO_2$ was obtained through $Na_{0.41}CoO_2$ crystal (20 mg) immersed in distilled water (120 ml) for about 120 hours. The actual Na concentration was determined by inductively coupled plasma spectrometer (ICP) chemical analysis. The detailed description on the synthesis and characterization of $Na_{0.34}(H_3O)_{0.15}CoO_2$, which is only sample to show the charge ordering behavior except for $Na_{0.5}CoO_2$, has been reported elsewhere.[17] The near-normal incident reflectance spectra were measured on the freshly cleaved surface by a Bruker 66 v/s spectrometer in the frequency range from 40~2900 cm^{-1}, as described in our early report.[20] Standard Kramers-Kronig transformations were employed to drive the frequency-dependent conductivity spectra. Susceptibility and magnetoresistance were measured in Quantum Design SQUID and PPMS system, respectively.

Fig. 1(a) shows temperature dependence of in-plane resistivity and susceptibility for $Na_{0.34}(H_3O)_{0.15}CoO_2$. As shown in Fig.1(a), similar insulating behavior to that in $Na_{0.5}CoO_2$ was observed below 50 K. It indicates that charge ordering behavior occurs in $Na_{0.34}(H_3O)_{0.15}CoO_2$. Susceptibility shows two transitions at 84 and 47 K. It is quite similar to that observed in $Na_{0.5}CoO_2$ although the transition temperatures are slightly lower compared to $Na_{0.5}CoO_2$. Oxidation state (3.49) of Co ions in $Na_{0.34}(H_3O)_{0.15}CoO_2$ is almost the same as that (3.50) in $Na_{0.5}CoO_2$. It suggests that the charge ordering in Na_xCoO_2 system strongly depends on the valence of Co ion. In comparison with $Na_{0.5}CoO_2$, differential curve $d\rho/dT$ was shown in Fig.1(b) and (c). A dip of the $d\rho/dT$ was observed at $T_{c1} \sim 84$ K, and the obvious change in the slope $d\rho/dT$ was also observed at $T_{c2} \sim 50$ K and $T_\rho \sim 10$ K, respectively. These features are quite similar to that in $Na_{0.5}CoO_2$, in which the dip is observed at $T_{c1} \sim 87$ K and the slope of $\rho(T)$ increases abruptly at $T_{c2} \sim 53$ K and $T_\rho \sim 20$ K.[2, 18, 19] It is commonly believed that the anomaly at $T_{c1} \sim 87$ K arises from an antiferromagnetic ordering.[12, 13] The anomaly at $T_{c2} \sim 53$ K is not clear although a kink is observed in susceptibility[2, 18] due to no change in magnetic structure drastically.[12] Dramatic change in $d\rho/dT$ at T_ρ is believed to arise from spin reorientation.[18] The behavior in $Na_{0.34}(H_3O)_{0.15}CoO_2$ crystal is similar to $Na_{0.5}CoO_2$ despite these anomalous temperatures are lower. Therefore, the origin for these anomalies in $Na_{0.34}(H_3O)_{0.15}CoO_2$ and $Na_{0.5}CoO_2$ should be the same.

To further characterize the charge ordering behavior in $Na_{0.34}(H_3O)_{0.15}CoO_2$, in-plane optical conductivity spectra are measured. As shown in Fig.1(d), in-plane optical conductivity spectra of $Na_{0.34}(H_3O)_{0.15}CoO_2$ are quite similar to that of $Na_{0.5}CoO_2$.[20] A broad hump appears below 100 K at about 800 cm^{-1} was observed.[20] A sharp suppression of the conductivity spectra below charge ordering temperature indicates an
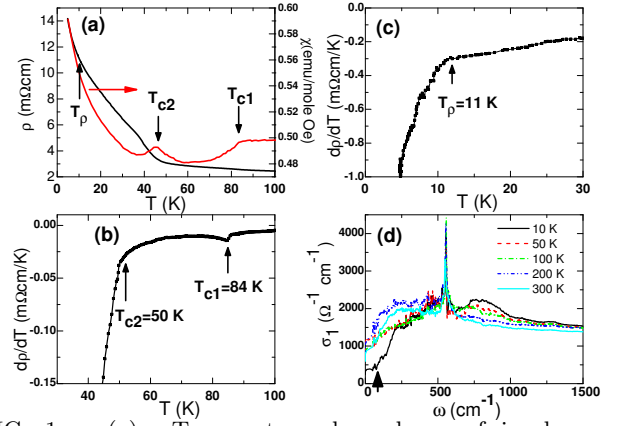

FIG. 1: (a): Temperature dependence of in-plane resistivity and susceptibility with H ∥ Co-O plane for $Na_{0.34}(H_3O)_{0.15}CoO_2$; Temperature dependence of the slope $d\rho/dT$ for the data shown in (a), (b): temperature range from 30 to 100 K; (c): the temperatures below 30 K; (d): In-plane optical conductivity spectra of $Na_{0.34}(H_3O)_{0.15}CoO_2$.

opening of charge gap. The gap value is close to the reported value of ~ 125 cm^{-1} with $2\Delta/k_B T_{co} = 3.5$.[20] It further indicates that all features observed in $Na_{0.5}CoO_2$ occur in $Na_{0.34}(H_3O)_{0.15}CoO_2$.

Fig. 2(a) shows isothermal in-plane MR at 5 K and 20 K with different α. The α is the angle between magnetic field H and current I. It can be seen that MR are negative at 5K and 20 K with $H\|I$ (within Co-O plane), while positive with $H\perp$ the Co-O plane. One should note that MR is almost zero with $\alpha = 90^o$ at 20 K. Such behavior has been observed in $Na_{0.5}CoO_2$.[19]
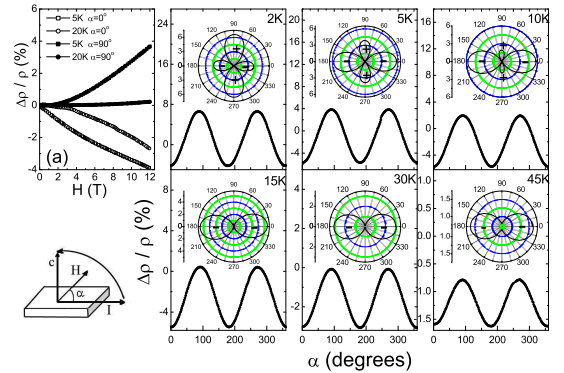

FIG. 2: (a): The isothermal MR at 5 K and 20 K with different angles between H and I; (b): The angular dependent isothermal MR and polar plot for $Na_{0.34}(H_3O)_{0.15}CoO_2$ under H=12 Tesla at different temperatures. The magnetic field H is kept in the plane consisting of the current and c-axis when the sample is rotated, as shown in schematic diagram.

In order to study effect of spin ordering on the charge transport (especially below T_ρ) and to understand the behavior observed in Fig.2(a), we investigated the angular

dependent in-plane MR behavior at different temperatures by rotating H in the plane consisting of the current and c-axis, as shown in schematic diagram. The magnetic field is fixed at 12 T during the measurement. As shown in Fig.2, the MR increases with decreasing temperature, and the magnitude of MR $\Delta\rho_{ab}/\rho_{ab}$ at 2 K is almost five times larger than that at 45 K. The data reveal that the AMR has two-fold symmetry above 15 K, and the MR is always negative and the maximum negative MR occurs at $\alpha=0$ and 180°, that is: the H lies in the Co-O plane. While the MR is almost zero with H perpendicular to the Co-O plane above 15 K. A striking feature is that the AMR shows clearly a symmetry evolution from p-wave-like to d-wave-like with decreasing temperature. One can observe only two negative arms above 15 K. Two small positive arms begin to be observed at 10 K. The two positive arms become large with further decreasing temperature, and eventually dominate at 2 K. With the growth of positive arms, one can find that the negative arms shrink slightly. It should be pointed out that the AMR symmetry transition from twofold to fourfold occurs at ~ 15 K close to T_ρ. Such fascinating transition was also observed at $T_\rho \sim 20$ K in $Na_{0.5}CoO_2$.[19] Such d-wave like behavior in AMR has been observed in antiferromagnetic $YBa_2Cu_3O_{6+x}$, and is believed as a consequence of the rotation of stripe direction with respect to the current direction.[21] Therefore, we believe that the evolution of AMR symmetry observed in charge ordering state should arise from change of magnetic structure under magnetic field.

AMR is also studied with rotating H in the Co-O plane. Fig.3 shows isothermal in-plane MR as a function of angle and the polar plot for $Na_{0.34}(H_3O)_{0.15}CoO_2$ at H=12 Tesla at different temperatures. The magnitude of MR increases approximately by 5 times at low temperature relative to that at 40 K. Similar to the case with rotating H in the plane consisting of the current and c-axis, symmetry of AMR is twofold above 15 K, but changes to sixfold at 2 K. The variation of MR with angle follows a sine wave above 15 K. The data at 15 K clearly show that peak and valley of the sine wave broaden and become asymmetry. It suggests that symmetry of AMR begins to change to sixfold at 15 K, which is consistent with the temperature corresponding to twofold to fourfold symmetry in AMR as shown in Fig.2. It implies that symmetry change of AMR in Fig.2 and Fig.3 arises from the same origin. Nevertheless, the data in Fig.3 exhibit some distinct difference from that in Fig. 2. Firstly, the MR remains negative at all angles in the whole temperature regime, and the magnitude of MR at each fixed angle always increases with decreasing temperature. Secondly, AMR shown in Fig.3 changes to six-fold at 2 K and exhibits obviously asymmetric, while AMR at various temperatures shown in Fig.2 is symmetric.

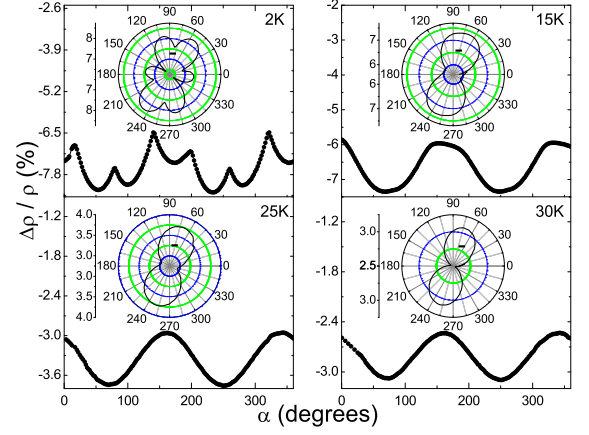Another striking feature is that the angle difference between neighboring peaks in AMR at 2 K shown in

FIG. 3: The isothermal MR as a function of angle for the $Na_{0.34}(H_3O)_{0.15}CoO_2$ at H=12 Tesla and the polar plot. H is kept in Co-O plane when the sample is rotated.

Fig.3 is exactly 60°. Therefore, such nice sixfold symmetry of AMR at 2 K seems to be related to the crystallographic structure because the crystal structure of Na_xCoO_2 is hexagonal. However, the sixfold symmetry of AMR with rotating H in Co-O plane is only observed below 15 K as shown in Fig.3. Therefore, such sixfold symmetry of AMR does not originate directly from the crystal structure. It should be pointed out that no such sixfold symmetry of AMR can be observed in other Na_xCoO_2 without charge ordering. It suggests that the symmetric feature of AMR observed in Fig.2 and Fig.3 could be related to the spin structure. Yokoi et al. proposed a magnetic structure shown in Fig.4 (a) and (b) for $Na_{0.5}CoO_2$. The spin structure has three axis, two axes are $Co^{3.5-\delta} - Co^{3.5-\delta}$ and the other one is $Co^{3.5+\delta} - Co^{3.5+\delta}$.[12] The large moments of $Co^{3.5+\delta}$ sites align antiferromagnetically at $T_{c1} \sim 87$ K with spin direction in Co-O plane. The small moments of $Co^{3.5-\delta}$ sites is along c-axis and their interplane correlation is antiferromangetic. It is difficult to distinguish their in-plane correlation, so that there exist two possibilities for the in-plane correlation as shown in Fig.4(a) and (b).[12] But they remain an open question that at what temperature the small moments of $Co^{3.5-\delta}$ sites order. The evolution of the AMR symmetry with temperature shown in Fig.2 and Fig.3 can be well understood by the spin structure proposed by Yokoi et al. At high temperature, the symmetry of AMR is twofold for both of the cases with rotating H in the Co-O plane and in the plane consisting of the c-axis and the current. This is because only the large moments of $Co^{3.5+\delta}$ sites order antiferromagnetically at high temperature. Therefore, only a "stripe"-like spin ordering along $Co^{3.5+\delta} - Co^{3.5+\delta}$ exists in the Co-O plane. It naturally explains the twofold symmetry of AMR shown in Fig.2 and Fig.3. For the case with rotating H in Co-O plane at high temperatures, we proposed a model for the
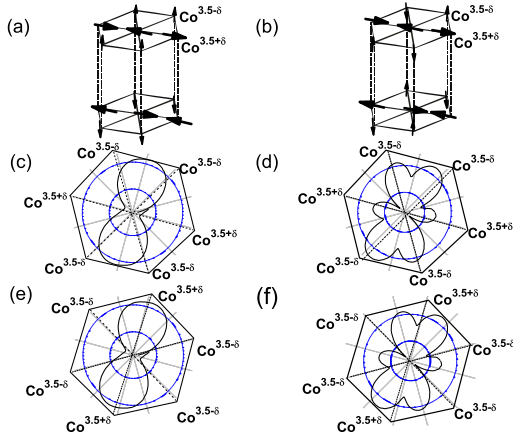
FIG. 4: (a) and (b): Possible magnetic structures proposed by Yokoi et al.[12] for $Na_{0.5}CoO_2$; (c) and (d): A possible configuration for the in-plane matching between the magnetic structure and the AMR symmetry at 15 and 2 K, respectively; (e) and (f): Another possible configuration for the in-plane matching between the magnetic structure and the AMR symmetry at 15 and 2 K, respectively.

matching between the AMR symmetry and the magnetic structure shown in Fig.4(c) and (e). There exist two possibilities for the relation between the AMR symmetry and magnetic structure: one is that the maximum MR occurs with H along the $Co^{3.5+\delta}-Co^{3.5+\delta}$ axis, the other is perpendicular to the $Co^{3.5+\delta}-Co^{3.5+\delta}$ axis. At low temperatures, the spin ordering at $Co^{3.5-\delta}$ sites with small moment occurs, and consequently the magnetic structure is hexagonal in the Co-O plane. Such hexagonal magnetic structure leads to the sixfold symmetry of AMR with rotating H in Co-O plane shown in Fig.3. The two possible correlations between the AMR symmetry and the magnetic structure are proposed in Fig.4(d) and (f) at low temperatures. Based on the observation of sixfold symmetry of AMR at 2 K shown in Fig.3, the magnetic structure prefers to that in-plane correlation for the magnetic moments at $Co^{3.5-\delta}$ sites is antiferromagnetic shown in Fig.4(b). This is because in-plane symmetry of the magnetic structure is not hexagonal if all the $Co^{3.5-\delta}$ sites are exactly equivalent as shown in Fig.4(a). The fourfold and twofold symmetries of AMR shown in Fig.2 can be also understood with the magnetic structures at low and high temperatures, respectively. Therefore, present results support the magnetic structure proposed by Yokoi et al.[12] The magnetic structure proposed by Gasparovic et al.[13] cannot explain the sixfold symmetry of AMR observed in Fig.3 because only a "stripe"-like spin ordering along $Co^{4+}-Co^{4+}$ occurs in Co-O plane in their model. A strong scattering of electrons from spins should occur with the current perpendicular to the antiferromagnetic "stripe" along $Co^{3.5+\delta}-Co^{3.5+\delta}$. However, it is difficult to distinguish which set of the configurations shown in Fig.4(c) and (d), Fig.4(e) and (f) is more realistic because

we cannot determine the $Co^{3.5+\delta}-Co^{3.5+\delta}$ axis. The evolution of the AMR symmetry with temperature shown in Fig.2 and Fig.3 suggests that the spin ordering of $Co^{3.5-\delta}$ sites with small moments occurs at ~ 15 K, which is close to the T_ρ. This is explained why the resistivity increases rapidly at T_ρ. It should be pointed out that symmetry change of AMR observed in $Na_{0.34}(H_3O)_{0.15}CoO_2$ can be also observed in $Na_{0.5}CoO_2$, only $T_\rho \sim 20$ K at which the ARM symmetry changes from twofold to sixfold is slightly different in Na_xCoO_2 x$\sim$ 0.5.[22]. These results give a good understanding on the transport and magnetic properties for the charge ordering Na_xCoO_2, especially on the anomalies at T_ρ, T_{c1} and T_{c2}.

In this letter, the angular-dependent in-plane magnetoresistance (AMR) for $Na_{0.34}(H_3O)_{0.15}CoO_2$ is systematically studied. The symmetry of AMR is twofold for both of the case with rotating H in the Co-O plane and in the plane consisting of the current and c-axis above T_ρ, while changes to sixfold and fourfold below T_ρ, respectively. These intriguing results support the magnetic structure proposed by Yokoi et al. We solve the open question for the spin ordering temperature ($\sim T_\rho$) of the small moments at $Co^{3.5-\delta}$ sites. The present work shows that the AMR is an auxiliary but powerful tool to study the subtle change of the magnetic structure. The magnetic and transport properties of $Na_{0.34}(H_3O)_{0.15}CoO_2$ are the same as those of $Na_{0.5}CoO_2$. It indicates intercalation of oxonium ions occurred and its charge compensation to make the oxidation state of Co to be close to ~ 3.5 when Na_xCoO_2 crystal was hydrated. Therefore, one should take the charge ordering insulator with Co oxidation state of ~ 3.5 as parent compound of the superconductor to think about superconducting mechanism and phase diagram.

* Corresponding author; Electronic address: chenxh@ustc.edu.cn
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